

Electrochemical Disinfection Feasibility Assessment Materials Evaluation for the International Space Station

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The International Space Station (ISS) Program recognizes the risk of microbial contamination in their potable and non-potable water sources. The end of the Space Shuttle Program limited the ability to send up shock kits of biocides in the event of an outbreak. Currently, the United States Orbital Segment water system relies primarily on iodine to mitigate contamination concerns, which has been successful in remediating the small cases of contamination documented. However, a secondary method of disinfection is a necessary investment for future space flight. Over the past year, NASA Johnson Space Center has investigated the development of electrochemically generated systems for use on the ISS. These systems include: hydrogen peroxide, ozone, sodium hypochlorite, and peracetic acid. To use these biocides on deployed water systems, NASA must understand of the effect these biocides have on current ISS materials prior to proceeding forward with possible on-orbit applications. This paper will discuss the material testing that was conducted to assess the effects of the biocides on current ISS materials.

Nomenclature

<i>ASTM</i>	= American Society for Testing and Materials
<i>CPP</i>	= cyclic potentiodynamic polarization
<i>CRES</i>	= Corrosion Resistant Steel
<i>DI</i>	= deionized
<i>DSC</i>	= differential scanning calorimetry
<i>ECD</i>	= electrochemical disinfection
<i>FT-IR</i>	= Fourier transform-infrared spectroscopy
<i>H₂O₂</i>	= hydrogen peroxide
<i>ICP-MS</i>	= inductively coupled plasma-mass spectrometry
<i>ISS</i>	= International Space Station
<i>L</i>	= liter
<i>mg</i>	= milligram
<i>mV</i>	= millivolt
<i>mpy</i>	= milli-inches per year
<i>NASA</i>	= National Aeronautics and Space Administration
<i>NaOCl</i>	= sodium hypochlorite
<i>PAA</i>	= peracetic acid
<i>PEEK</i>	= Polyether Ether Ketone

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<i>PC</i>	= polycarbonate
<i>PP</i>	= polypropylene
<i>s</i>	= second
<i>SCC</i>	= stress corrosion cracking
<i>TGA</i>	= thermogravimetric analysis
<i>Ti-6Al-4V</i>	= titanium
<i>V</i>	= volt

I. Introduction

The electrochemical disinfection (ECD) feasibility assessment began in late 2011 and was completed in March 2013. The project explored four different biocides that could be generated in situ and potentially used as a disinfectant in on-orbit water system applications. Hydrogen peroxide (H_2O_2), sodium hypochlorite ($NaOCl$), peracetic acid (PAA), and ozone were investigated to understand their capability at reacting with bacteria, to determine their responses to materials and chemicals found on the International Space Station (ISS), and finally to gain knowledge of the different physical and chemical properties in solution.¹ This paper focuses on the materials testing that was conducted during the ECD feasibility assessment.

The ISS potable water system, as well as other water-related hardware, is comprised of various materials. Introducing a new chemical or material to the current system could impact existing operations should any interactions occur. Over the course of a year, various testing was conducted on both metallic and non-metallic materials that have been identified on the ISS. Long-term immersion testing and cyclic potentiodynamic polarization (CPP) testing were conducted on metallic specimens. Short-term immersion testing was conducted on non-metallic specimens. An overview of material selection, test methodology and setup, test results, and recommendations for forward work will be discussed in this paper.

II. Material Selection

An analysis was conducted to identify materials currently used in the ISS potable water system, as well as water-related hardware. Specifically, materials that were considered part of the wetted portion of the water system were scrutinized for applicability in the ECD feasibility assessment testing. Initially, a total of 12 metallic and 19 non-metallic materials were identified as wetted materials on-orbit. Materials that were determined to be of like quality had one material representative for testing. Additionally, an extensive literature review was executed to find existing information on the identified materials and compatibility with the selected biocides. This downselection provided a representative set of materials that was investigated against H_2O_2 , PAA, $NaOCl$, and ozone.

A total of eight metallic materials were chosen as a representative set of ISS water system metallic materials. The eight materials, along with their finished state and test participations, are listed below:

- 1) Corrosion Resistant Steel (CRES) 316 (passivated, tested in all immersion and CPP test conditions)
- 2) CRES 430F (passivated, tested in all immersion and CPP test conditions)
- 3) CRES 302 (passivated, tested in all immersion and CPP test conditions)
- 4) CRES A286 (passivated, tested in all immersion and CPP test conditions)
- 5) CRES 15-5PH (passivated, tested in all immersion and CPP test conditions)
- 6) Titanium (Ti-6Al-4V) (not passivated, tested in all immersion and CPP test conditions)
- 7) Hastelloy C-276 (not passivated, tested in all immersion and CPP test conditions)
- 8) CRES 17-7PH (passivated, tested in CPP test conditions only)

A total of six non-metallic materials were selected as a representative set of ISS water system non-metallic materials. The materials selected either had questionable compatibility at higher biocide concentrations, or did not have supporting compatibility data for the particular biocide. The six materials are listed below:

- 1) High Density Polyethylene
- 2) Polycarbonate (PC)
- 3) Polypropylene (PP)
- 4) Polyether Ether Ketone (PEEK 450G)
- 5) Viton[®]
- 6) Delrin[®] 150

A non-metallic filter material was identified in the ISS water system. Hydrophillic Nylon 6,6 was tested due to lack of data available for the selected biocide concentrations. A slightly different test method was used for the filter material. Metallic specimens underwent long-term immersion testing (12 months) and CPP testing. Non-metallic specimens underwent a short-term immersion test (14 days). Various measurement techniques were used to obtain an understanding of compatibility concerns. Test plans were developed for each compatibility test, which included test methods and data collection.

III. Test Methodology and Setup

All materials testing was conducted with commercially available biocides. The ECD feasibility assessment was successful at electrochemically generated biocides; however, due to schedule constraints, materials compatibility testing was conducted with the following commercially procured biocides: H_2O_2 , NaOCl, PAA, and ozone.

A total of four different tests were performed to assess the compatibility of materials with the four biocides. The four tests were comprised of two types of test methods: immersion and CPP. Immersion testing was conducted on metallic materials, non-metallic materials, and hydrophillic Nylon 6,6. CPP testing was conducted on metallic materials only. The following paragraphs will discuss the specific test methodology and setup associated with the four test methods.

A. Metals Material Testing

1. Immersion

Immersion testing was performed on the representative ISS water system alloys to determine general corrosion rates and susceptibility to crevice corrosion and stress corrosion cracking (SCC) from the biocide solutions. A 3-, 6-, and 12-month immersion test was conducted. All immersion tests used 1-liter (L) containers filled to $1 \text{ L} \pm 0.1 \text{ L}$ of biocide solution. Deionized (DI) water was used as a control solution for comparison to the biocide solutions. Ozone in solution has approximately a 15-minute lifetime, and therefore is difficult to maintain for long durations. Due to this challenge, ozone was not tested in metals immersion testing. The biocide test solutions in this program were as follows:

- 1) H_2O_2 at 1000 milligrams (mg)/L $\pm 100 \text{ mg/L}$
- 2) NaOCl at 10 mg/L $\pm 1 \text{ mg/L}$
- 3) PAA at 180 mg/L $\pm 19 \text{ mg/L}$

Monthly change outs were conducted for all biocide solutions and the DI water control solution during the course of immersion testing. During solution change outs, measurements of biocide concentration, dissolved oxygen, and pH were taken from each container, and samples were taken to evaluate the presence of dissolved metals in each solution using inductively coupled plasma-mass spectrometry (ICP-MS). The test vessels were kept in a dark location to avoid biocide degradation from light exposure (Fig. 1).

Three sets of corrosion test specimens were tested for each alloy/solution combination, with each set consisting of triplicate corrosion rate specimens and one crevice corrosion specimen. Each alloy/solution combination was tested in its own container. One specimen set was removed for analysis at 3, 6, and 12 months of test duration. Separate containers were used for each SCC specimens. These containers held four U-bend SCC specimens that were observed monthly and continued to be tested in desired solutions.

The corrosion testing was performed in accordance with American Society for Testing and Materials (ASTM) G1 and ASTM G31. Corrosion rates were calculated per ASTM G1, section 8, with positive corrosion rates indicating mass loss; negative corrosion rates indicated mass gains. Corrosion specimens were observed upon



Figure 1. Metal immersion test setup.

removal, weighed, cleaned, and weighed again. The rates discussed in the results section are the average of the three general corrosion specimens in each vessel after the posttest cleaning was conducted. Crevice corrosion testing used the crevice washer configuration from ASTM G48, and was performed in the same solutions and temperatures (room temperature) as the general corrosion testing. SCC susceptibility was tested using U-bend specimens based on ASTM G30, and in the same solutions and temperatures as the general corrosion testing, but in different containers than other corrosion testing.

2. Cyclic Potentiodynamic Polarization

CPP is an electrochemical technique known to determine whether a metal will be subject to pitting corrosion during immersion in an aqueous solution. In this method, cathodic and anodic potentials are applied to a metal sample, and the corresponding current response is measured. The current response is related to the electrochemical and corrosion reactions that occur on the metal surface, primarily pitting and passivation. For this study, CPP testing was performed on all metal types in each of the four biocide solutions to determine whether the biocides would induce surface pitting, which could eventually lead to cracking of metal components. The test biocides in this solution were as follows:

- 1) H_2O_2 at 1000 mg/L
- 2) NaOCl at 10 mg/L
- 3) PAA at 180 mg/L
- 4) Ozone at 1 mg/L

A copper lead wire was attached to each metal sample to create an electrical connection for the electrochemical testing, and the bare metal areas that were not being measured for pitting were electrically isolated to avoid polarization of the entire sample and connector configuration. Each exposed sample surface was polished up to 1200 grit, nearly a mirror finish. The prepared samples were cleaned using methanol, and photographed using a metallographic microscope prior to CPP testing. Each sample was immersed in a biocide solution, along with an appropriate supporting electrolyte, 2.3 mg/L sodium sulfate, until steady state occurred in a 1 L glass container. For the dissolved ozone solution, the ozone was added to the electrolyte via a commercial ozone generator using a ceramic fritted bubbler. All metal types were tested in a solution of only the supporting electrolyte to verify CPP results as a function of biocide type. A potentiostat was used to apply a potential sweep from -0.01 volt (V) to 1.2 V to -0.05 V versus the open circuit potential of each metal and electrolyte combination. The scan rate was 0.5 millivolt (mV)/second (s), and a graphite counter electrode and standard calomel reference electrode were used (Fig. 2).

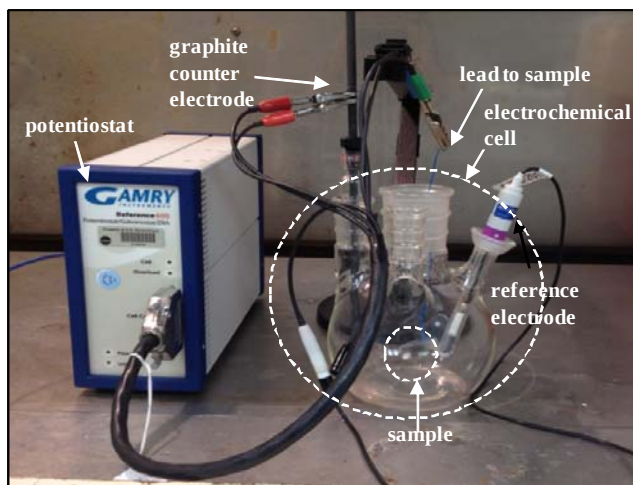


Figure 2. Cyclic potentiodynamic polarization test setup.

Forty unique metal and biocide combinations were tested in triplicate. After the CPP testing, the data were analyzed for evidence of pitting corrosion. The samples' surfaces were examined using a metallographic microscope and dye penetrant analysis to physically identify pitted areas and verify the CPP results.

B. Non-Metals Material Testing

The non-metal materials were immersed in the biocide solutions to determine degradation as a function of immersion time. For H_2O_2 , PAA, and NaOCl biocides, the samples were immersed in sealed Nalgene[®] containers for 14 consecutive days and stored in the dark under ambient laboratory conditions. For the dissolved ozone solution, the samples were immersed in glass electrochemical cells and ozone was bubbled through DI water for 14 nonconsecutive 8-hour periods. These samples were suspended in the cells, and the cells were not sealed. The cells

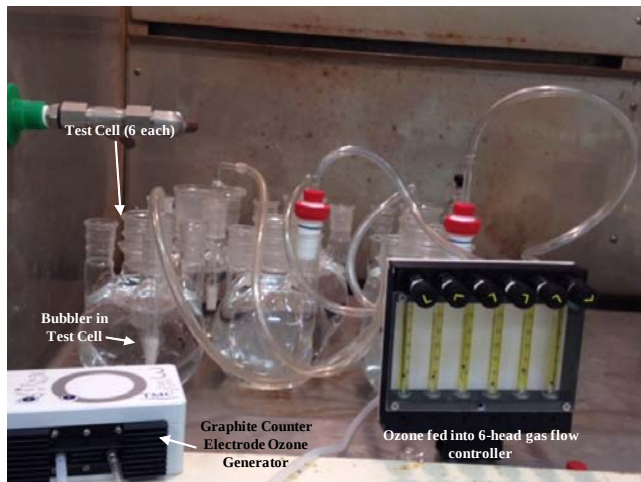


Figure 3. Ozone non-metals test setup.

were stored out of direct ultraviolet light; however, they were not stored in dark conditions (Fig. 3).

All of the non-metal types, with the exception of Nylon 6,6, were immersed in DI water, dissolved ozone, and the 180mg/L PAA solution. The Delrin[®] 150 was also immersed in H_2O_2 and NaOCl . The PEEK 450G was additionally immersed in a solution of 2000 mg/L of PAA. Prior to and after immersion, the non-metal materials underwent physical and chemical testing to determine degradation effects of the biocides. Testing included mass, dimensional measurements, hardness, visual inspection, and optical microscopy, Fourier transform-infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). FT-IR was used to determine oxide changes on the sample surface due to degradation; the TGA and DSC were used to

determine events associated with degradation such as changes in weight as a function of temperature and changes in melting and phase transition temperatures. Each non-metal type was tested in triplicate, and the physical and chemical testing was performed on one set of materials exposed only to ambient laboratory conditions.

Hydrophillic Nylon 6,6 underwent a similar duration of non-metals immersion testing; however, since this material is used as a filter, measurement of degradation used a bubble point integrity test. This particular test measures the applied pressure required to penetrate through the largest filter pores, causing bulk or open poreflow. The defined bubble point of a material is indicated by a steady flow of gas across the filter. Testing was conducted with compressed nitrogen. Specimens were immersed in 10 mg/L NaOCl , 180 mg/L PAA, and 1000 mg/L H_2O_2 for 14 consecutive days. A total of two control samples were maintained during the course of this testing. One specimen was immersed in DI water. The second specimen was maintained at atmospheric conditions (no immersion).

IV. Results

A. Metals Material Results

1. Immersion Test Results

Immersion testing was ongoing at the time of publication; therefore, 12-month results are not captured in this paper. Deionized water served as the control solution for all alloys that were tested. No corrosion products, pitting, or staining was observed on the specimens upon removal after 3 or 6 months of testing, and corrosion rates were very low, less than 2×10^{-3} milli-inches per year (mpy). After undergoing the specimen cleaning process, all DI water specimens returned to an appearance similar to what they started with prior to testing. The DI water solutions did not induce crevice corrosion on any specimens. SCC testing was not performed on the DI water specimens since ISS water system materials are not susceptible to SCC in DI water.

Upon removal from the H_2O_2 , the 3- and 6-month Ti-6Al-4V, Hastelloy C-276, CRES A286, and CRES 430F specimens showed discoloration. The discoloration of the alloys was more prevalent in the 6-month specimens than the 3-month specimens, with the exception of the Ti-6Al-4V. After undergoing the cleaning process, all H_2O_2 specimens, with the exception of the Ti-6Al-4V and C-276 specimens, returned to their pre-test appearance (Fig. 4). The caustic cleaner was unable to completely remove the rust-colored deposits from the CRES 430F (although the majority of the deposits on those specimens were removed). ISS water system materials are not susceptible to SCC in H_2O_2 , therefore SCC was not tested. The average 6-month corrosion rates for the H_2O_2 specimens are shown in

Fig. 6. After cleaning, all alloys except Ti-6Al-4V showed mass losses. CRES 430F, CRES A286, and Hastelloy C-276 showed particularly significant corrosion rates when compared to the other alloys in H_2O_2 , corresponding well with the alloys that tinted or discolored visually. An increase in weight was seen in the Ti-6Al-4V specimen. ICP-MS analysis of dissolved metals in the H_2O_2 solutions correlated well with the corrosion rate data for the various alloys. Solutions tested from the CRES alloys 302, 316L, and 15-5PH did not produce significant dissolved metals, whereas CRES 430F, CRES A286, and Hastelloy C-276 alloying elements were present in their test solutions.

Upon removal from the NaOCl solutions, heavy rust was clearly visible on the CRES 430F specimens; the Hastelloy C-276 specimens had a significant yellow tint. The CRES 430F specimens displayed heavy rust over the majority of the specimen surfaces, with heavy deposits adjacent to and underneath the Teflon[®] spacers and crevice washers (Fig. 5). The deposits and tinting were more pronounced at the 6-month test duration. Small rust spots were present on two CRES 302 specimens adjacent to the crevice created by the Teflon[®] spacers at 6 months. After caustic cleaning of the specimens, Hastelloy C-276 and Ti-6Al-4V regained their before-test appearance. No corrosion products, pitting, or staining was observed on the CRES 316, CRES A286, or CRES 15-5PH specimens. After cleaning, heavy pitting was found on all CRES 430F specimens due to crevice corrosion caused by the specimens' Teflon[®] spacers. The CRES 430F and Hastelloy C-276 specimens showed significant corrosion rates both before and after cleaning. ICP-MS analysis of dissolved metals in the NaOCl solutions correlated well with the corrosion rates for the alloys tested. The solutions from CRES alloys 302, 316, and 15-5PH, as well as the CRES A286 and Ti-6Al-4V alloys, contained negligible dissolved metals. The CRES 430F solutions contained high amounts of iron and chromium in solution, along with minor amounts of manganese. The Hastelloy C-276 solutions contained consistently high amounts of nickel, chromium, and molybdenum. The dissolved metals in solution represent the primary alloying elements for those alloys. No SCC specimens cracked during the 6-month exposure to NaOCl at 10 mg/L.

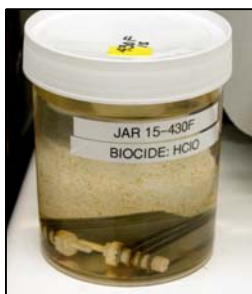


Figure 5. Rust particulates in test vessel of NaOCl and CRES 430F at 6 months.

holes of the CRES 430F specimens, but were easily removed by the caustic cleaner. As such, the possibility of crevice corrosion for longer test durations is a possibility. The average 3-month corrosion rates for the PAA specimens are shown in Fig. 6. CRES 302 and Ti-6Al-4V specimens showed modest weight gains, whereas CRES 316L, CRES 430F, and Hastelloy C-276 produced negligible changes. CRES A286 had a low to moderate post-cleaning corrosion rate, whereas CRES 15-5PH showed a moderate to high corrosion rate post-cleaning. ICP-MS analysis of dissolved metals in the PAA solutions showed negligible results. Several alloys showed low concentrations of their primary alloying elements, but almost all values were below 100 mg/L. No SCC specimens cracked during the 3-month exposure to PAA at 180 mg/L.

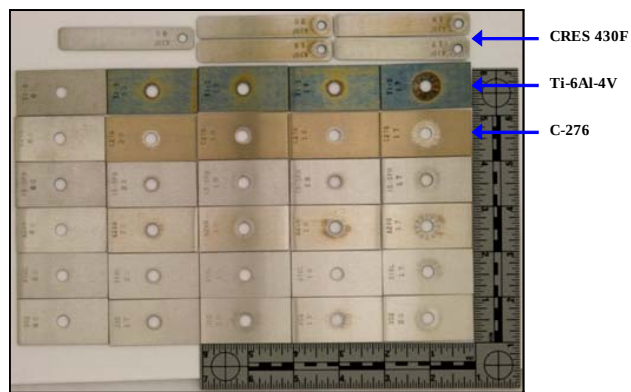


Figure 4. Hydrogen peroxide 6-month post cleaning specimens.

Testing for 180 mg/L PAA commenced 3 months after the other solutions and was completed to 3 months at the time this paper was written. Small amounts of non-adherent rust were present in the fastener

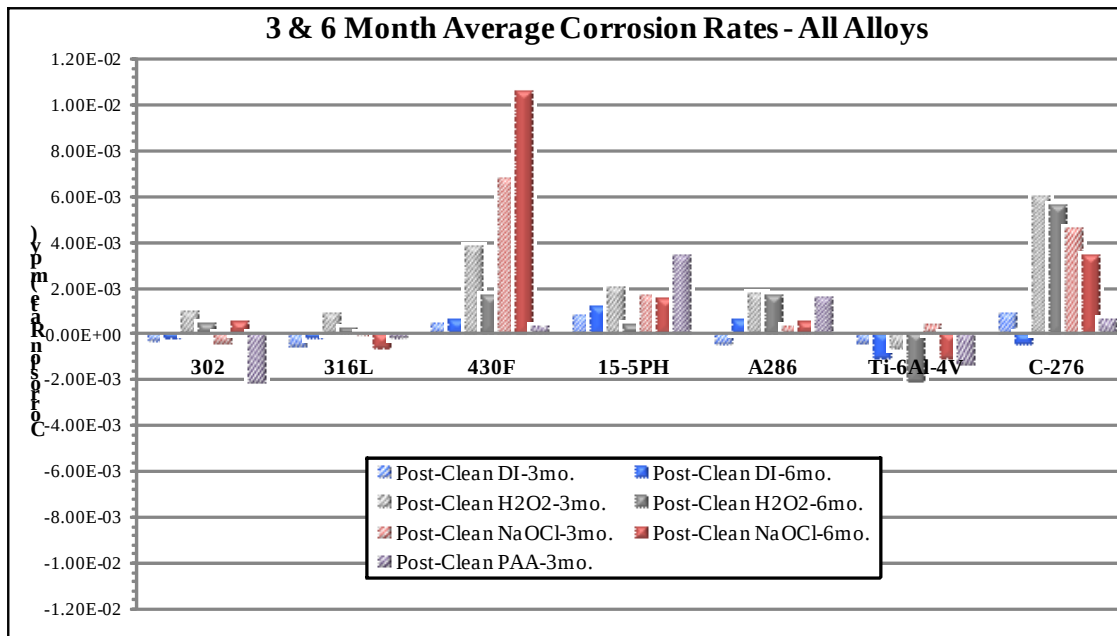


Figure 6. Average corrosion rates (3 and 6 month) for metallic specimens.

2. Cyclic Potentiodynamic Polarization Test Results

For all of the biocide solutions, some form of corrosion, either localized pitting or general, was identified on the metal surface for the majority of the metal types. General corrosion, either in the form of surface etching or in the form of a corrosion oxide film, was the most common type of corrosion found on the surfaces. No pitting or corrosion was identified on the metals tested in the supporting electrolyte solution with no biocide (control specimen).

Localized pitting was identified on the surfaces of CRES 17-7PH, CRES 430F, and CRES A286, and general corrosion occurred for Hastelloy C-276 and CRES 302 in the NaOCl solution. Pitting was detected on CRES 316 after CPP testing in PAA, whereas general corrosion was identified on CRES 15-5PH, Hastelloy C-276, CRES 302, CRES 430F (Fig. 7), and CRES A286.

Pitting was identified on the surfaces of CRES 17-7PH, CRES 430F, and CRES A286 in the dissolved ozone solution, whereas general corrosion was observed on Hastelloy C-276, CRES 302, and CRES 316. CRES15-5PH had no net change after exposure to the CPP test in the dissolved ozone.

The H₂O₂ biocide solution did not induce pitting corrosion; however, for CRES 316, general corrosion was formed in localized areas that could lead to the possible induction of pitting corrosion. All of the steel metal samples showed signs of general corrosion after exposure to CPP testing in the H₂O₂ solution.

Although each metal type behaved differently for each biocide solution, general behaviors were found. The alloys CRES 17-7PH, CRES 316, CRES 430F, and CRES A286 were the most susceptible to pitting. Alloys CRES 15-5PH, Hastelloy C-276, and CRES 302 did not show any signs of pitting, but rather showed general surface etching and oxide layer formation. The titanium alloy, Ti-6Al-4V, did not show signs of any form of corrosion. The H₂O₂ solution was the least aggressive biocide type according to CPP testing. The PAA, dissolved ozone, and NaOCl biocide solutions were more aggressive, especially for CRES 430F and CRES A286 alloy types.

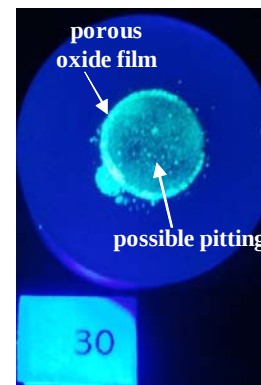


Figure 7. Fluorescent photographic exposure of CRES 430F in PAA.

B. Non-Metals Material Results

In general, for the non-metals results, physical properties like dimensions, weight, and hardness did not vary much compared to exposure to DI water. Degradation was identified by visible changes and corresponding FT-IR analysis of oxide state changes. Changes in mass loss via TGA and glass transition temperatures via DSC were indicative of more aggressive degradation. No degradation was observed for non-metals immersed in DI water (except Viton®), 2000 mg/L PAA, H₂O₂, and NaOCl solutions. Nominal degradation occurred for PC, Viton®, and PP samples immersed in the 180 mg/L PAA solution. The Viton® samples had the most significant changes observed through visual inspection and FT-IR, but they may or may not be significant compared to the behavior of Viton® in DI water. Degradation was observed for all of the non-metals immersed in dissolved ozone with the exception of PEEK 450G. The surface layer was visually degraded for the Delrin® 150 samples after immersion in the dissolved ozone, and degradation was noted through both FT-IR, TGA, and DSC analysis. The surface layer of the PC samples exhibited crazing and degradation through FT-IR analysis. Table 1 is a summary of material degradation results for each non-metal and biocide combination.

Table 1. Material degradation summary for non-metals immersed in biocides.

Biocide Type	HDPE	PC	PEEK 450G	Viton®	Delrin® 150	PP
H ₂ O ₂	n/a	n/a	n/a	n/a	No Change	n/a
180 mg/L PAA	No Change	Degradation	No Change	Degradation	No Change	Degradation
2,000 mg/L PAA	n/a	n/a	No Change	n/a	n/a	n/a
NaOCl	n/a	n/a	n/a	n/a	No Change	n/a
Ozone	Degradation	Degradation	No Change	Degradation	Degradation	Degradation
DI Water	No Change	No Change	No Change	Localized Degradation	No Change	No Change

n/a = not applicable

The hydrophillic Nylon 6,6 immersion testing showed minimal to no changes when immersed in the three different biocides. Sodium hypochlorite and PAA showed a decrease in biocide concentration over the course of the test, but minor deviations from the established bubble point were measured. The three biocides do not appear to have an impact on the integrity of the filter material.

V. Conclusion

The testing performed underneath the ECD feasibility assessment concluded that H₂O₂, NaOCl, PAA, and ozone all have compatibility issues with at least one identified ISS water system material. Future testing should take into consideration using electrochemically generated biocides to determine whether additional or different compatibility concerns are present. Biocides produced electrochemically have the potential for other chemical constituents to be present, therefore potentially changing the compatibility with various materials. It is critical to understand the compatibility issues with electrochemically generated biocides, to design, implement, and successfully operate a disinfectant on the ISS or future exploration vehicles. It is recommended that the extensive data set produced during the ECD feasibility assessment be used as a starting point for the design and development of future water-systems for space flight.

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